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To cite this version:
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(Received 6 June 1990, accepted 11 September 1990)

Abstract. — Grain boundaries in intermetallic compounds such as Ni$_3$Al are inherently brittle. The reason is usually sought in grain boundary cohesion but in metals even brittle fracture is accompanied by some local plasticity and thus not only cohesion but also dislocation mobility in the boundary region need to be studied. We first discuss here the role of an irreversible shear deformation at the crack tip during microcrack propagation assuming that these two processes are concomitant. It is shown that a pre-existing crack cannot propagate in a brittle manner once the dislocation emission occurs. However, if a microcrack nucleates during loading it can propagate concurrently with the development of the irreversible shear deformation at the crack tip. The latter is then the major energy dissipating process. In the second part of this paper we present results of atomistic studies of grain boundaries in Ni$_3$Al and Cu$_3$Au which suggest that substantial structural differences exist between strongly and weakly ordered L1$_2$ alloys. We discuss then the consequence of these differences for intergranular brittleness in the framework of the above model for microcrack propagation. On this basis we propose an explanation for the intrinsic intergranular brittleness in some L1$_2$ alloys and relate it directly to the strength of ordering.
1. Introduction.

In pure metals grain boundaries are not generally susceptible to brittle cracking and when fracture occurs it frequently takes the form of transgranular cleavage. Intergranular fracture is usually associated with segregation of embrittling impurities to grain boundaries and it is, therefore, observed in alloys, such as ferritic steels, nickel based alloys etc. (for reviews see, for example [1-5]). This suggests that in pure metals, with an exception of iridium [6, 7], grain boundaries are not regions which are weaker than the bulk of the material. On the other hand, recent studies of the mechanical properties of intermetallic compounds suggest that grain boundaries in these alloys may be intrinsically brittle. The fact that intermetallic compounds are often less ductile than pure metals and disordered alloys is not surprising, in particular if they crystallize in low symmetry structures in which the number of available slip systems is limited. However, intergranular fracture occurs readily in the face-centered-cubic based L12 compounds, such as Ni3Al, although these materials are ductile as single crystals. On the other hand, Cu3Au which possesses the same structure, is always ductile. In Ni3Al the intergranular brittleness has been observed for both stoichiometric and off-stoichiometric concentrations [8, 9] and no significant segregation of some embrittling elements to the grain boundaries has been found to accompany the fracture process. At the same time intergranular fracture can be suppressed by alloying with boron which segregates to grain boundaries (for recent reviews see [10-12]).

When analyzing the material brittleness from a microscopic point of view it is usually assumed that the most important parameter is the ideal work to fracture, 2γ, identified with the work to separate (usually reversibly) the material along a fracture path against atomic cohesion. In the case of intergranular cracking it is identified with 2γs - γb, where γs is the excess (free) energy per unit area of the surface formed during cracking and γb the excess (free) energy per unit area of the grain boundary. The influence of alloying on intergranular fracture is then sought in its effect upon these two quantities. However, in most metallic materials dislocations can move relatively easily even at low temperatures and brittle fracture is accompanied by a localized plastic flow [13-15]. Indeed, two alternate explanations of the intrinsic brittleness in Ni3Al and effects of boron have been put forth. The first is the suggestions that brittleness results principally from electronic effects [8, 10, 12, 16-19]. The other proposal is that the intergranular brittleness is related to the dislocation mobility in the grain boundary region. For example, a distinctly lower value of the Hall-Petch slope was observed in the material ductilized by boron than in the undoped material [20, 21] and recent electron microscope observation indicate that slip near the boundaries is easier in the presence of boron [22, 23].

In ductile materials fracture and localized plasticity cannot be regarded as two exclusive processes and it can be assumed, therefore, that some incipient dislocation-like irreversible shear deformation occurs simultaneously with the bond breaking and dissipates a significant part of the energy. This can account for the observations that the work of fracture associated with extension of microcracks is often more than an order of magnitude larger than 2γ [24-26]. However, as first pointed out in [27], this « plastic » work and the ideal work to fracture are mutually dependent since reduced cohesion that permits bond breaking at lower stresses must also result in a reduced crack tip dislocation activity. The model of such a process, originally developed by Jokl et al. [28-30], is discussed in the first part of this paper. It is shown that a clear distinction needs to be made between pre-existing and injected cracks. While the concomitant bond breaking and dislocation emission can take place in the latter case, in the former case any dislocation activity inhibits fracture. The model, of Rice and Thomson [31, 32], which regards bond breaking and dislocation emission as exclusive processes, applies in this case.
Since we find that the cohesion and the dislocation mobility in the vicinity of the microcrack are equally important parameters when analyzing intergranular fracture, effects of structure and chemistry on both of them must be considered. Our present understanding of these phenomena is still rather rudimentary and no quantitative analyses are available. In this paper we first discuss briefly the possible effects of alloying on the intergranular cohesion in compounds both from a thermodynamic point of view and by considering possible electronic effects. However, in these approaches structural aspects of grain boundaries are not considered while these are essential when analyzing dislocation mobility in the boundary region (see e.g. [33]). For this purpose we present results of the recent calculations of the structure of grain boundaries in Ni$_3$Al and Cu$_3$Au. While both these alloys crystallize in the L1$_2$ structure they possess very different ordering energies and we show here that this is the main reason for the significant differences in their boundary structures. We then discuss potential differences in dislocation mobilities in the vicinity of grain boundaries in these alloys and their relation to the intergranular brittleness.


Let us consider first an externally loaded body with a microcrack and investigate whether bond-breaking and irreversible shear deformation may occur simultaneously at the crack tip. Thus we consider a crack tip which is inelastically distorted by localized shears within a few atomic spacings of the tip which lead to dissipation of energy and add in this way to the work of fracture. We describe these shears as dislocation emission but recognize that the Burgers vector associated with the shear on any given crystallographic plane intersecting the crack tip may be smaller than that of a lattice dislocation. We presume that after the crack tip passes a given point, these dislocations fall back to the crack faces and disappear. It is important to emphasize that we do not deal with an elastic crack shielded by lattice dislocations and/or by a macroscopic plastic zone. The latter would correspond to the propagation of a brittle macroscopic crack through a material that responds to the crack stress field by producing plastic deformation at distances hundreds or thousands of atomic spacings away from the crack tip. This problem has been recently treated in references [34, 35].

Owing to the external loading a stress intensity factor, $k$, is associated with the microcrack. The basic thermodynamic criterion determining the critical stress intensity factor, $k_c$, at which the microcrack propagates, is the Griffith criterion [36] for unstable crack extension which includes now not only the ideal work to fracture, $2\gamma$, but also the energy dissipated by the irreversible shears, $W_p$. Hence, this criterion reads:

$$- G(k) + 2\gamma + W_p(k, \beta) \leq 0 \quad (1)$$

where $G(k)$ is the elastic energy release rate. The «plastic» work $W_p$ is not a constant as, for example, in the Orowan's treatment of incorporation of the plastic work into the fracture criteria [37], but a function of $k$, and a parameter $\beta$ which measures the ease of irreversible shearing at the crack tip; in the dislocation description of the shearing process $\beta = v_d/c$, where $v_d$ is the velocity of emitted dislocations and $c$ the shear wave velocity. The principal task is now to evaluate $W_p$ as a function of $k$ and solve equation (1) to obtain $k_c$ as a function of $\gamma$ and $\beta$.

A simplified model of the propagating microcrack which is at the same time emitting dislocations from its tip has recently been developed by Jokl et al. [30] assuming Mode III loading. For this mode solutions can be obtained much more easily than for Mode I or II and yet the main features of the solutions are the same as for the other modes. In this model the inelastic shearing at the crack tip is represented by a single screw Volterra dislocation located
at a distance $x(t)$ from the crack tip, the Burgers vector of which, $\Delta(t)$, increases as it moves away from the tip with the velocity $v_d$ under the influence of the stress $\sigma(t)$, evaluated at $x(t)$. The stress at a point $x$ in time $t$ due to a moving screw dislocation with a time dependent Burgers vector is

$$\sigma(x, t) = \int_0^t \left[ \frac{d\Delta(t')}{dt'} \Gamma(x, t; x', t') + \Delta(t') v_d \frac{\partial \Gamma}{\partial x'} \right] dt' \tag{2}$$

where $\Gamma$ is the Green's function for the creation of a screw dislocation ahead of a crack at time $t'$ at the position $x'$; it was derived in reference [30]. $\Delta(t)$ and $x(t)$ are determined from the requirement that there is no stress singularity at the crack tip i.e. that

$$\sigma_c^b(t, x \rightarrow 0) + \sigma_c^d(t, x \rightarrow 0) = 0 \tag{3}$$

where $\sigma_c^b$ is the singular part of the crack field and $\sigma_c^d$ is the singular part of the dislocation field. This implies that the stress ahead of the crack varies only slowly. The energy per unit area of crack extension dissipated by the shears is then

$$W_p = \frac{1}{b} \int_0^b \sigma(t) \left[ x(t) \frac{d\Delta(t)}{dt} + \Delta(t) v_d \right] dt \tag{4}$$

where $b$ is the increment of crack extension per broken bond and $t_b$ is the time required to break the bond between the atom pair at the crack tip. A model addressing the same type of problem has also been developed by Argon [38] but the criterion for crack propagation was formulated in terms of attaining a critical stress ahead of the crack. A more detailed analysis of the differences between the two models has been given in reference [30].

2.1 PRE-EXISTING CRACK. — We assume now that a sharp crack is present in the material which is loaded by a shear wave $\sigma = \tau H(ct - y)$ moving at velocity $c$ in the direction $y$, perpendicular to the crack surface; $H$ is the Heavyside step function. This represents the highest possible rate of loading. In a linear elastic solid the stress field ahead of the crack loaded in this way is known [30, 39] and its singular part is $\sigma_c^b = \frac{2 \tau}{\pi} (ct/x)^{1/2}$. Since the crack-tip stress is high, the emitted dislocations are assumed to be moving at their terminal velocity; hence $v_d$ is assumed constant. Exact analytical solution of equation (3) can be found in this case and it is [30] $\Delta(t) = \Delta_1 t$, where $\Delta_1$ is a function of $\beta$ and thus constant for a given value of $v_d$. When evaluating the stress at the dislocation using this solution it was found [30] that it does not depend on time. Owing to the cancelation of the singularity at the crack tip the stress ahead of the crack varies only slowly and, therefore, at the crack-tip the stress is also practically time independent as soon as dislocation emission commences. Hence, it cannot continue to rise beyond this point and crack propagation cannot take place.

The above analysis shows that if the propagation of a pre-existing crack is to occur, bond breaking must appear at some stress below that at which the dislocation emission starts. A criterion for brittle vs. ductile behavior of materials, based on the assumption that dislocation emission from a pre-existing crack precludes any subsequent brittle fracture, was first formulated by Kelly et al. [40] in terms of a balance between yield and fracture stresses. More recently this concept has been developed in terms of dislocation emission by Rice and Thomson [31, 32] and by Mason [41]. In this approach a critical stress intensity factor, $K_{\text{cr}}^d$, for dislocation emission is first found from the balance of repulsive force acting on the dislocation due to the crack stress and attractive image and ledge forces. This is then compared with the usual Griffith's critical stress intensity factor for brittle fracture,
The critical value of the microcrack stress intensity factor is determined by the condition (1) in which, for Mode III loading and crack propagating at a velocity $v_c$, $G = k^2(1 - \psi)/2 \mu$. This gives

$$k_c = \frac{k_c^{GR}}{[1 - \Phi(\beta, \psi)]^{1/2}}$$

where $k_c^{GR} = (4 \gamma \mu)^{1/2}/(1 - \psi)$ is the Griffith's critical stress intensity factor for brittle fracture controlled by the ideal cohesive strength; the factor $(1 - \psi)$ accounts for the non-zero rate of crack growth. $\Phi(\beta, \psi)$ is a numerically determined function of $\beta$ and $\psi$. For the case of $\psi = 0.3$, which corresponds to the crack moving at about one third of the speed of sound, $\Phi$ is shown as a function of $\beta$ in figure 1.

Fig. 1. — The dependence of $\Phi$ on $\beta$ calculated numerically in reference [30] for $\psi = 0.3$. 

$k_c^{GR}$, equal to $[4 \gamma \mu (1 - \nu)]^{1/2}$ in the case of Mode I loading; here $\mu$ is the shear modulus and $\nu$ the Poisson ratio. Fracture occurs then when $k_c^d > k_c^{GR}$. Unfortunately the value of $k_c^d$ depends sensitively on the radius of the dislocation core in the close vicinity of the crack tip and could only be properly determined by atomistic studies of dislocation emission from the crack tip. However, Lin [42] has shown that this criterion is physically equivalent to that of Kelly et al. [40].

2.2 INJECTED CRACK. — The principal characteristics of the injected crack is that the material is already fully loaded when at time $t = 0$ a new crack appears. The emission of irreversible shear from the crack tip commences at the moment of entry to the material. Such a situation arises whenever the crack is nucleated after the material has been loaded and the most common type of injected crack is that which originates at a brittle inclusion, as originally proposed by Zener [43] and McMahon and Cohen [44]. When treating this problem we also require that there is no stress singularity at the crack tip at any time $t > 0$ and thus equation (3) again determines $\Delta(t)$ and $x(t)$. However, the singular part of the crack stress field is now

$$\sigma_c^2 = (1 - \psi)^{1/2} \frac{k}{(2 \pi x)^{1/2}}$$

where $\psi = v_c/c$ is the normalized velocity of the crack. Using the approximation of constant dislocation velocity, an analytical solution of equation (3) has again be found [30]; $\Delta$ is now proportional to $k/\sqrt{ct}$ and the stress at the dislocation, $\sigma(t)$, is proportional to $k/\sqrt{ct}$ with the proportionality factors dependent on $\beta$. Using these values of $\Delta$ and $\sigma(t)$ and the relationship $v_c = b/\rho_{0}$, the dissipated energy, $W_p$, can be evaluated as a function of $k$ and $\beta$ according to equation (4). The critical value of the microcrack stress intensity factor is determined by the condition (1) in which, for Mode III loading and crack propagating at a velocity $v_c$, $G = k^2(1 - \psi)/2 \mu$. This gives
It is seen from equation (5) and figure 1 that when $\beta \rightarrow 0$, i.e. when no irreversible shear deformation occurs, $k_c$ attains the usual Griffith's value. However, as $\beta$ increases, $k_c$ increases rapidly above the Griffith's value and becomes infinite for a value of $\beta$ slightly above 0.6. This means that at this point the brittle fracture becomes impossible. However, for lower values of $\beta$ the injected crack, unlike the pre-existing one, can propagate in a brittle manner while irreversible shear deformation occurs at the crack tip. The corresponding values of $k_c$ are, of course, much higher than those determined on the basis of the ideal work to fracture, $\gamma$, since a large amount of energy is dissipated by the shearing process. It was further shown in reference [30] that if the dislocation velocity, $v_d$, is an increasing function of the stress then for each value of $\beta$ there is also a critical value of $\gamma$ above which $k_c$ would become infinite and thus no fracture could occur. Hence, the material fracture behavior is now characterized by two parameters, $\gamma$ and $\beta$. The latter can be taken as a measure of the ease of formation of inelastic shear at the crack tip while the former characterizes the strength of bonds. The value of $k_c$ for which an injected microcrack will propagate through a deformable material depends on both of them and it is particularly sensitive to $\beta$. This implies that a decrease in the ease of formation of inelastic shears may have a larger embrittling effect than the same decrease in the strength of bonds and, therefore, when considering effects of alloying on the intergranular brittleness it is essential to investigate not only its influence on grain boundary cohesion but also on the ability to produce local irreversible shear deformation in the boundary region.

3. Intergranular brittleness in intermetallic compounds.

3.1 Cohesion at grain boundaries. — Intergranular cohesion, described by the ideal work to fracture $\gamma$, is the physical quantity which may be controlling the intrinsic brittleness of intermetallic compounds even when a substantial irreversible deformation occurs in the vicinity of grain boundaries. This parameter has, of course, been always considered to be the most important one when analyzing embrittling phenomena and the goal of most of the analyses has been to establish a relationship between $\gamma$ and the interfacial chemistry. A general fundamental understanding of this relationship based on the electron theory of solids is still missing and most analyses are of phenomenological nature. A thermodynamical approach to this problem has been developed by Rice and co-workers [45-47] assuming that $2\gamma$ can be identified with the ideal work of reversibly separating an interface. When segregant divides equally on the two newly formed surfaces, $2\gamma = 2\gamma_0 - (\Delta g_b^0 - \Delta g_s^0) c_{seg}$ where $2\gamma_0$ is the work needed to separate a clean interface, $\Delta g_b^0$ and $\Delta g_s^0$ are Gibbs free energies of segregation (inherently negative) to the grain boundary and free surface, respectively, and $c_{seg}$ is the concentration of the segregant at the grain boundary. The embrittlement ensues then when $\Delta g_b^0 > \Delta g_s^0$, i.e. when segregation to free surfaces is preferred over segregation to grain boundaries, and it has been shown in [47] that this condition is, indeed, satisfied for many well known embritters of steels. In the opposite case, when $\Delta g_b^0 < \Delta g_s^0$, the segregant will decrease interfacial brittleness.

While these considerations cannot explain the intrinsic brittleness of grain boundaries in intermetallic compounds, they may be used to assess the effects of deviations from stoichiometry and segregation. For example, the ductility of the polycrystalline Ni$_3$Al can only be improved by boron alloying in Ni rich alloys and several recent observations suggest that segregation of Ni to grain boundaries, possibly together with boron [48, 49], takes place. At the same time no segregation of nickel to the surfaces has been reported. Similarly, boron segregates strongly to grain boundaries but not to surfaces [7, 50]. According to the above mentioned criterion both the boron and nickel segregation to grain boundaries should, indeed, increase the cohesion and thus improve the ductility.
The first systematic study of the effect of chemical factors on intergranular brittleness in L1₂ compounds has been made by Takasugi and Izumi [8, 10, 12, 16] who concluded that the tendency for intergranular fracture increases with increasing valency difference of the constituent elements. On the other hand, Taub and Briant [17-19] found that intergranular brittleness can be better correlated with the difference in electronegativity rather than valency. This empirical correlation has been interpreted in terms of a model originally proposed to explain the influence of impurities on intergranular cohesion [51, 52]. In this model the minority element B that is more electronegative than the majority element A, withdraws some electron density from the A-A metallic bonds. This is then regarded as the reason for weakening of the cohesion. However, this approach, based on cluster calculations, has recently been criticized as being inapplicable to metals because they display perfect screening of charges [53]. Hence, while the empirically established relations between the propensity for intergranular brittleness and electronegativity or valency differences between constituent elements have been used with a considerable success to predict effects of alloying on ductility of L1₂ compounds [10, 12, 18], an appropriate microscopic understanding of these phenomena is still elusive.

3.2 Atomic Structure of Grain Boundaries and Its Relation to Britteness. — In the above mentioned analyses of the intergranular cohesion it is implicitly assumed that the atomic structure in the boundary region is different from that in the bulk but it is not taken into account explicitly. At the same time it is plausible that there are some specific features of the grain boundary structure in compounds which are responsible for their intrinsic brittleness. In recent years a number of atomistic computer modeling studies of grain boundaries in L1₂ alloys have been performed with the aim to elucidate their general features and investigate grain boundary cohesion (e.g. [54-57]). These calculations were carried using the embedded atom method (EAM) [58] with potentials constructed such as to reproduce a number of measured properties of pure Ni and Al as well as Ni-Al alloys [59]. The energies of grain boundaries and free surfaces in Ni₃Al were found to be very similar to those in Ni. Thus there is no obvious reason why the ideal work to fracture should be very different in Ni₃Al when compared with pure Ni. Calculations investigating the effect of boron upon the cohesion of grain boundaries in Ni₃Al have also been made recently. Chen et al. [60, 61] used an EAM method with boron-metal interactions described by a potential which fits data obtained from quantum mechanical LMTO calculations for a number of hypothetical structures. Masuda-Jindo [62, 63] employed a simplified tight-binding method to investigate the boundary cohesion. Both these calculations suggest that boron increases the cohesive strength at the interface but the observed increase of the ideal fracture stress needed for separation of the material along the grain boundary is less than ten percent. However, an interesting finding of the calculations in references [62, 63] is that boron attracts nickel, favoring thus the co-segregation to grain boundaries, and in Ni rich boundaries the ideal fracture stress is then appreciably higher.

In order to investigate possible structural features which might be responsible for the intrinsic grain boundary brittleness in some L1₂ compounds, we have carried out a comparative study of grain boundaries in pure f.c.c. metals and L1₂ alloys. Originally this study was performed using pair-potentials describing stable L1₂ structures [64]. More recently, many-body Finnis-Sinclair type potentials [65] have been constructed for Ni₃Al and Cu₃Au. Using the method described in detail in reference [66], grain boundary studies have been carried out using these potentials. This allows us not only to compare structures of boundaries in pure metals and ordered compounds but to make a comparison of the atomic structures of boundaries in two different L1₂ alloys which exhibit very different fracture behavior. While Ni₃Al is intergranularly brittle, Cu₃Au is always ductile. The principal
differentiation between the two compounds reflected in the potentials is a large difference in
the ordering energies. Cu$_3$Au is a weakly ordered alloy with an order-disorder transformation
well before melting while Ni$_3$Al is a strongly ordered compound which stays ordered up to
melting. The ordering propensities are reflected in the energies of antiphase boundaries
(APB). Using the above mentioned many-body potentials the energies of 1/2[110](111) APB
are 54 mJm$^{-2}$ and 226 mJm$^{-2}$ for Cu$_3$Au and Ni$_3$Al, respectively.

In the case of Ni$_3$Al all the atoms in the boundary region can be regarded as uniquely
attached to either the upper or the lower grain so that the ideal L1$_2$ structure is almost
undisturbed on either side of the boundary up to the boundary plane. Hence only very small
local relaxation of atoms in the boundary region takes place; a substantial rigid body
translation of the grains relative to each other may, however, occur. One consequence of the
lack of the local relaxation is the presence of columns of atomic size cavities in these
boundaries. These features of the grain boundaries are exhibited in figures 2 and 3 which
show the structures of the $\Sigma = 5(310)$ and $\Sigma = 73(830)$ symmetrical tilt boundaries with [001]
rotation axis, calculated using the potentials for Ni$_3$Al. The same structural features were
found in our calculations using pair potentials to describe the atomic interactions in L1$_2$ alloys
[64] and can be seen in the results of all the previous EAM calculations [67].

![Fig. 2. Structure of the $\Sigma = 5(310)$/[001] symmetrical tilt boundary in Ni$_3$Al. In this and the following pictures crosses and triangles represent atoms belonging to different (002) layers, shading distinguishes different species and the repeat cell of the boundary is marked by solid lines.](image)

![Fig. 3. Structure of the $\Sigma = 73(830)$/[001] symmetrical tilt boundary in Ni$_3$Al.](image)
On the other hand, in pure f.c.c. metals and in Cu$_3$Au the relaxation in the boundary is considerable and in a narrow region of the boundary the atoms cannot be clearly assigned to either the upper or to the lower grain. The distribution of atoms in the boundary region is much more homogeneous than in the case of Ni$_3$Al. This is seen in figures 4 and 5 which show the structures of the $\Sigma = 5(310)$ and $\Sigma = 73(830)$ boundaries, calculated using the potentials for Cu$_3$Au. Since the structures of the same boundaries in pure Cu or Ni are very similar to those shown in figures 4 and 5 they are not presented here separately. The reason for these remarkable structural differences can be sought in differences in ordering energies. In the case of a high ordering energy (Ni$_3$Al), the chemical order is the principal factor controlling the energy of the system. Its preservation dominates the grain boundary structure. On the other hand, in the case of a low ordering energy (Cu$_3$Au) more relaxed grain boundary structures, similar to those in pure f.c.c. metals, are energetically favored over those in which the order is preserved at the expense of a significant inhomogeneity in the boundary region. This relaxation may then provoke a substantial chemical disorder in the boundary region.

The preservation of the ideally ordered L1$_{\text{b}}$ structure up to the grain boundary plane and the resulting lack of the local atomic relaxation in the boundary region leads to the presence of columnar cavities in grain boundaries in Ni$_3$Al. This is in contrast to pure f.c.c. metals and also Cu$_3$Au, where the distribution of atoms in the boundary region is much more homogeneous. Owing to the «openness» of the boundary structures in strongly ordered alloys the overall intergranular cohesion might be weaker but it was found in the previous

![Fig. 4. — Structure of the $\Sigma = 5(310)/[001]$ symmetrical tilt boundary in Cu$_3$Au.](image)

![Fig. 5. — Structure of the $\Sigma = 73(830)/[001]$ symmetrical tilt boundary in Cu$_3$Au.](image)
atomic studies that this is not a very significant effect [54, 55, 57]. However, the columnar cavities may serve as nucleation sites for microcracks which are then much more likely to be formed at grain boundaries in strongly ordered alloys. As discussed in section 2.2, the propagation of such injected microcracks is then principally controlled by the parameter $\beta$ describing the ease with which local irreversible shear deformation may occur in the boundary region. The lattice resistance for such a shearing process can be expected to be much higher in strongly ordered alloys than in the weakly ordered ones. The reason is that in the former case the ideally ordered L1$_2$ structure extends up to the boundary and a high energy APB is formed during shearing. On the other hand, in the weakly ordered alloys the region of the boundary may be structurally, and also chemically, disordered so that no APB is formed during the localized shearing and even if the order is preserved, the energy of the corresponding APB is much lower. Similarly, the transmission of the dislocations through the boundary is likely to be easier in the disordered case as suggested in [48, 68]. The calculated atomic structures of grain boundaries thus suggest that nucleation and subsequent propagation of intergranular cracks in strongly ordered L1$_2$ alloys is much easier than either in pure f.c.c. metals or in weakly ordered alloys.


In the first part of this paper we have shown that in deformable materials a microcrack may propagate in the brittle manner while localized irreversible shear deformation occurs simultaneously at its tip. However, this is only possible if the microcrack has been nucleated during loading and thus, effectively, a moving crack enters already fully loaded metallic material. The localized shear deformation developing in the close vicinity of the crack tip is then the most important energy dissipating mechanism. The critical microcrack stress intensity factor, $k_c$, then depends on two material parameters, the ideal work to fracture, $\gamma$, and the rate of inelastic shearing in the vicinity of the crack path, $\beta$. The latter is, generally, a function of the stress near the crack tip and if it exceeds a critical value, the brittle fracture is no more possible. On the other hand, a pre-existing crack can propagate in the brittle manner only if bond breaking occurs prior to any crack tip deformation. In the opposite case the ensuing dislocation emission will blunt the crack. The value of $k_c$ is then determined by the criterion [31, 40] according to which fracture occurs if the stress needed for cracking is attained, at least locally, before the yield stress is reached.

Since there is no reason why cracks should be present at the grain boundaries in intermetallic compounds such as Ni$_3$Al prior to loading, the inherent brittleness of these compounds is most probably associated with propagation of cracks which nucleate upon loading. Thus the case of an injected microcrack is relevant in the studies of this problem. The atomistic studies of the structure of grain boundaries in L1$_2$ alloys show that in alloys with a high ordering energy (Ni$_3$Al) the ideally ordered structure tends to be preserved up to the grain boundary plane. This causes that columnar cavities are present in grain boundaries and those may serve as suitable nuclei for microcracks. When the ordering energy is low (Cu$_3$Au) the distribution of atoms in the boundary region is more homogeneous and similar to that in f.c.c. metals. Furthermore, as discussed in the previous section, the lattice resistance for inelastic shearing in the boundary region will be higher in strongly ordered alloys than in the weakly ordered ones. Hence, $\beta$ is likely to be significantly lower in the former case so that brittle fracture is more likely to occur.

On the basis of these considerations we conclude that the intrinsic brittleness of grain boundaries in certain L1$_2$ compounds is directly related to their strength of ordering. However, the ordering energy alone can only be taken as the most important parameter controlling the propensity to intergranular fracture of compounds and not the only factor. If,
for example, segregation of one of the components of the alloy occurs even when the bulk composition is stoichiometric, the boundaries may not be inherently brittle since they will then resemble boundaries in disordered alloys. This tendency was found in our previous calculations [64] of boundaries in which a substantial deviation from the L1_2 stoichiometry exists. Whether a segregation of this type occurs or not does not depend only on the ordering energy; other chemical and electronic effects have to be considered. This may also be the main reason why alloying with boron suppresses the intergranular brittleness. As suggested by recent observations [48, 49] and calculations [60, 61] co-segregation of boron and Ni to grain boundaries may be taking place in Ni_3Al, particularly if in the off-stoichiometric form with a surplus of Ni. This will lead to the decrease of the chemical and structural order in the boundaries, and following the above arguments, it will decrease the propensity to intergranular cracking.

Acknowledgements.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Grant n DE FG02-87ER45295.

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